Selective, Active Catalytic Nanoparticle Arrays Fabricated

An MSD team led by Gabor Somorjai and Eric Anderson has used state-of-the-art lithography to fabricate arrays of catalytic sites with finely controlled shape and size. Catalyst function on these nanofabricated arrays was compared to that found on industrial catalysts, leading to new insights concerning the influence of active site geometry on activity and selectivity.

It has been known since the 1920's that the nanometer-scale structure of the active site of a catalyst determines critical aspects of its function, in particular, activity and selectivity. In principle, an active site with the correct geometry should be able to provide 100% selectivity for the desired reaction product. Catalysts used in industrial hydrocarbon processing typically consist of nanometer-scale metal particles dispersed on a high surface area, porous, oxide support. Parameters such as the size and density of the metal particles, their surface composition, and the nature of the oxide support and the metal-oxide interface can profoundly affect the function of these catalysts. The physical processes involved include adsorption, chemical reaction(s), and desorption of the reactant and product species; all of these can occur at different rates at different locations (e.g. metal surface, metal/oxide interface, etc.) in the catalyst. For this reason, much effort has been devoted to tuning catalyst function by depositing the metal under different processing conditions. However, because the particle sizes vary, it has not been possible to precisely control the geometry of the active site and thus achieve the desired catalytic selectivity.

The MSD team has approached this problem by using state-of-the art electron beam lithography techniques to build platinum-based catalysts. The great advantage of this approach is that particle size and interparticle distance (pitch) can be controlled precisely. The team used MSD's Nanowriter facility at the Center of X-Ray Optics to make an array of 10^9 20-nm platinum particles with 100 nm spacing on a 0.5 cm^2 SiO_2 substrate (see figure). They chose as their model catalytic system the conversion of cyclohexene to either cyclohexane or benzene. The reaction conditions can be controlled to determine which of these two possible products is favored: increased pressure favors the addition of hydrogen, and the production of cyclohexane; increased temperature favors the removal of hydrogen, favoring benzene production.

The team first compared the reactivity of the Pt/SiO_2 array with a bulk platinum foil for cyclohexene conversion to benzene at 100 °C. The overall reactivity of the platinum nanoparticle array was twice as high as that of the platinum foil. The selectivity towards dehydrogenation was three times higher, and the rate of catalyst deactivation was about the same. Since the primary difference between the nanoparticle array and the platinum foil is the interface between the platinum and the SiO_2, the team concluded that the interfacial region is most likely responsible for the changes in selectivity on the arrays.

The team is currently working to systematically vary the particle size and interparticle distance to determine their effects on the performance of the nanoparticle arrays. Its goal is to build models of "high technology" catalysts that are stable at high temperatures, resistant to poisoning, 100% selective and long-lived, thus providing energy savings and waste reduction. Successful implementation of this research has far-reaching scientific as well as industrial implications.

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A. Avoyen, G. Rupprechter, A. S. Eppler, and G. A. Somorjai, "Fabrication and characterization of the Ag-based high-technology model nanocluster catalyst for ethylene epoxidation manufactured by electron beam lithography," *Topic in Catalysis* **10**, 107-113 (2000).